

## PATENT SPECIFICATION

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## (54) BIOCIDAL COMPOSITIONS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LTD., Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to biocidal compositions and more particularly to compositions comprising certain isothiazolin-3-ones and quaternary ammonium compounds.

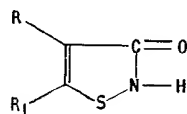
UK Patent Specification No. 884541 relates to a process for the protection of aqueous media against infection by micro-organisms by adding to the aqueous media a 1,2-benzisothiazolin-3-one which may be substituted in the benzene ring by chlorine or bromine or salts thereof.

UK Patent Specification No. 1224663 describes the preparation of certain 3-hydroxyisothiazoles (which are tautomeric with isothiazolin-3-ones) and the biocidal applications of these compounds.

Our copending UK Application No. 22353/73 (Serial No. 1460279) describes complexes and mixtures of isothiazolin-3-ones with long chain alkyl quaternary ammonium compounds and their use as biocides.

It has now been found that complexes and mixtures of poly (quaternary ammonium) compounds with isothiazolin-3-ones are also useful as biocides.

According to the present invention there are provided biocidal compositions comprising a polymeric quaternary ammonium compound as hereinafter defined and isothiazolin-3-ones compound having the general formula



40 wherein

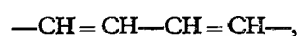
R represents a hydrogen atom, a halogen atom, a C<sub>1</sub>—C<sub>4</sub> alkyl group or a cyano group;

R<sub>1</sub> represents a C<sub>1</sub>—C<sub>4</sub> alkylsulphinyl

group, an aralkylsulphinyl group containing up to 8 carbon atoms, a C<sub>1</sub>—C<sub>4</sub> alkylsulphonyl group or an aralkylsulphonyl group containing up to 8 carbon atoms when R is a cyano group;

R<sub>1</sub> represents a hydrogen atom, a halogen atom, an aralkyl group containing up to 8 carbon atoms or a C<sub>1</sub>—C<sub>4</sub> halogeno alkyl group when R is a C<sub>1</sub>—C<sub>4</sub> alkyl group or a halogen atom provided that R<sub>1</sub> can be a C<sub>1</sub>—C<sub>4</sub> alkyl group when R is a C<sub>1</sub>—C<sub>4</sub> alkyl group and R<sub>1</sub> is an aralkyl group containing up to 8 carbon atoms or a C<sub>1</sub>—C<sub>4</sub> halogeno group when R is a hydrogen atom; or

R and R<sub>1</sub> taken together represent the divalent group



the hydrogen atoms of which may be replaced by substituents selected from halogen atoms, C<sub>1</sub>—C<sub>4</sub> alkyl groups, C<sub>1</sub>—C<sub>4</sub> alkoxy groups, the nitro group and the cyano group.

Examples of isothiazolin - 3 - ones which may be used are 1,2 - benzisothiazolin - 3 - one and its 5- and 6-chloro and 5 - methyl derivatives.

By polymeric quaternary ammonium compounds we mean any polymeric compound containing a plurality of quaternary ammonium groups, for example, homopolymers of monomeric quaternary ammonium compounds having at least one group capable of vinyl polymerisation attached to the quaternary nitrogen atom and inter-polymers of two or more different monomeric quaternary ammonium compounds of this kind or of at least one such monomeric quaternary ammonium compound with at least one other monomer containing at least one group which is copolymerisable therewith. Further useful polyquaternary ammonium salts are those which can be prepared by the Menshutkin reaction between a bistertiary amine and a bishalo compound. Salts of this latter type are known as ionenes. Polyquaternary ammonium salts may also be prepared by reaction of a polymer containing reactive halogen atoms

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with one or more tertiary amines or conversely by reaction of a polymer containing tertiary amine groups by reaction with one or more halogen compound.

5 Examples of monomeric quaternary ammonium compounds from which polymeric compounds may be prepared are trimethyl 2-methacryloyloxyethyl ammonium chloride, vinylbenzyl trimethyl ammonium chloride, diallyl dimethyl ammonium chloride, dimethyl ethyl 2 - methacryloyloxyethyl ammonium methosulphate, trimethyl 2 - hydroxy - 3-methacryloyloxypropyl ammonium bromide, dimethyl 2 - hydroxyethyl 2 - methacryloyloxyethyl ammonium chloride, trimethyl 2 - acryloyloxyethyl ammonium iodide, dimethyl hydroxypropyl 2 - acryloyloxyethyl ammonium chloride, N - methylvinylpyridinium chloride, trimethyl 3 - acrylamidopropyl ammonium chloride, dimethyl benzyl 3 - methacrylamidopropyl ammonium bromide, trimethyl vinyloxycarbomethyl ammonium chloride, trimethyl vinyloxyethyl ammonium chloride, diallylmethyl  $\beta$  - propionamido ammonium chloride and 1 - vinyl - 3 - methylimidazolium methosulphate.

30 Examples of compounds which are not monomeric quaternary ammonium compounds but which contain at least one group which is copolymerisable therewith are styrene, vinyl toluene, methyl methacrylate, ethyl acrylate, vinyl acetate, acrylamide, methacrylamide, acrylonitrile, divinyl benzene and ethylene glycol dimethacrylate. Diallyl dialkyl ammonium salts may also be copolymerised with sulphur dioxide.

40 Examples of polymeric quaternary ammonium compounds which can be used in formulating compositions according to the present invention are 60 : 40 molar copolymer of styrene and trimethyl 2 - methacryloyloxyethyl ammonium chloride, poly (trimethyl 2-methacryloyloxyethyl ammonium methosulphate), poly (vinylbenzyl trimethyl ammonium chloride), cyclic polymer of diallyl dimethyl ammonium chloride, poly (N-methyl vinyl pyridinium chloride), poly (vinyl chloro acetate) quaternised with pyridine, copolymers of poly (vinyl chloroacetate) and vinyl acetate quaternised with pyridine and the polymer from decamethylene dibromide and N,N,N',N' - tetramethyl hexamethylene - diamine.

55 The polymeric quaternary ammonium salts can be prepared by methods which are well described in the scientific literature. The range of polymeric quaternary salts available and relevant methods of preparation have been reviewed by H. F. Hoover in Journal of Macromolecular Science-Chemistry 1970, A4 (6), 1327—1417.

65 The hydrogen atom of the NH group in the isothiazolin - 3 - one ring system is acidic, and salt-like chemicals complexes are formed between isothiazolin - 3 - ones and quaternary

ammonium compounds. It will be evident that not all of the quaternary ammonium groups in a polymeric quaternary ammonium compound as hereinbefore defined need be involved in salt formation with the isothiazolin - 3 - one compound. Some only of the total number of quaternary ammonium groups may be so involved, the others remaining untreated. The compositions of the present invention therefore include the cases in which the isothiazolin - 3 - one is present in excess or in deficit over the amount necessary to complex with all of the quaternary ammonium groups in the polymeric quaternary ammonium compound. The relative amounts of the polymeric compound and the isothiazolin-3-one compound in the composition according to the present invention may therefore be varied widely, and these two components may be used respectively in proportions by weight in the range 50 : 1 to 1 : 50, but preferably in the range 5 : 1 to 1 : 5.

The biocidal compositions of the present invention may be prepared by mixing appropriate portions of the polymeric quaternary salt and the isothiazolin - 3 - one either dry or as aqueous solutions or suspensions. Solutions or suspensions in media other than water may be used if desired. Sodium or other alkaline earth or an amine salt of the isothiazolin-3 - one may be used. The mixture in the media in which they have been prepared may be used without further treatment. However, the complex or polymeric quaternary salt and the isothiazolin - 3 - one may be separated by filtration, where it is insoluble in the media, or by evaporation of the media, or by other suitable isolation method and used in that form.

The compositions have the advantage over isothiazolin - 3 - ones used alone in that the biocidal efficiency of the isothiazolin - 3 - ones is improved by the co-use of a polymeric quaternary ammonium compound even where the latter has little or no biocidal effect on its own.

Other advantages are that in the circumstances in which isothiazolin - 3 - ones are fairly readily removed from the substrates to which they are applied and thus rendered ineffective, for example by being leached out on exposure to rain, compositions according to the present invention may have reduced mobility and are thus more persistent; also, compared with isothiazolin - 3 - ones, the compositions may be so formulated as to have improved compatibility with certain substrates. For example, the composition can be made compatible with oils by the use of a polymeric quaternary ammonium compound obtained by copolymerising a quaternary monomer with a non-quaternary oleophilic co-monomer. Furthermore, skin-irritant properties and mammalian toxicity of compositions according to the present invention may be reduced com-

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pared with the isothiazolin - 3 - ones from which they are derived.

The preferred isothiazolin - 3 - one compound is 1,2 - benzisothiazolin - 3 - one.

5 The biocidal compositions find application as bactericides and fungicides, particularly in an aqueous media, for example, in water/oil emulsions, in-can preservation of water-based paints and adhesives and in cooling water systems; also as paint-film fungicides and in preventing fungal attack on wood. The compositions are also effective in the presence of anionic compounds, for example, soap, which is not compatible with quaternary ammonium compounds.

15 Thus, the present invention also provides a method for protecting aqueous media against infection by micro-organisms, and for controlling or preventing the proliferation of micro-organisms in aqueous media already

infected thereby, which comprises adding to the aqueous media from 1 to 1000 parts per million by weight of a biocidal composition comprising a polymeric quaternary ammonium compound and an isothiazolin - 3 - one compound as hereinbefore described.

The two components may be added independently to the aqueous medium if desired.

The invention is illustrated but not limited by the following example.

#### Example.

A 1 ml. sample of an aqueous suspension of an overnight agar culture of *Pseudomonas aeruginosa* was added to 100 ml. of test biocide solution in a 250 ml. conical flask incubated at room temperature. Samples were removed at intervals and the surviving bacteria were determined. The results are summarised in the following table:—

Experiment No.	Biocidal Solution		Surviving Bacteria (Bacterial Cells/ml.) after			
	Agent	Concentration (p.p.m.)	2 hours	3 hours	4 hours	6 hours
1	None		$>3 \times 10^7$	$>3 \times 10^7$	$>3 \times 10^7$	$>3 \times 10^7$
2	BIT	100	$>3 \times 10^7$	$>3 \times 10^7$	$>3 \times 10^7$	$>3 \times 10^7$
3	BIT	200		$>3 \times 10^7$		$1.6 \times 10^7$
4	BIT	1000	$7 \times 10^5$		$1.5 \times 10^5$	0
5	S/TMMAC	100	$1.6 \times 10^7$		$2.7 \times 10^6$	$1.9 \times 10^5$
6	S/TMMAC	1000	$8.2 \times 10^6$		$8.4 \times 10^6$	$8.2 \times 10^6$
7	TMMAM	100	$4 \times 10^7$		$3.5 \times 10^7$	$1.8 \times 10^7$
8	TMMAM	1000	$4.3 \times 10^5$		$1.9 \times 10^4$	$1.6 \times 10^3$
9	PVBTAC	200		$5 \times 10^5$		$<10$
10	PVBTAC	1000		90		$<10$
11	cyclo PDDAC	200		$1.6 \times 10^7$		$<10$
12	cyclo PDDAC	1000		$8 \times 10^3$		$<10$
13	S/TMMAC + BIT	100 + 100	$4.6 \times 10^4$		$3.4 \times 10^3$	$5 \times 10^2$
14	TMMAM + BIT	100 + 100	$3.6 \times 10^5$		$8.6 \times 10^3$	70
15	PVBTAC + BIT	100 + 100		$<10$		$<10$
16	cyclo PDDAC + BIT	100 + 100		$<10$		$<10$

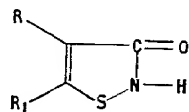
In the above table Experiments Nos. 1-12 are comparative experiments; Nos. 13-16 are examples according to the present invention.

In the above Table, BIT=1,2 - benzisothiazolin - 3 - one; S/TMMAC=60:40 molar copolymer of styrene and trimethyl 2 - methacryloyloxyethyl ammonium chloride; TMMAM=poly(trimethyl 2 - methacryloyloxyethyl ammonium methosulphate); PVBTAAC=poly(vinylbenzyl trimethyl ammonium chloride); cyclo PDDAC=cyclic polymer of diallyl dimethyl ammonium chloride.

The advantageous effect obtained by using the isothiazolin - 3 - one compound and the polymeric quaternary ammonium compound together, as compared with their use individually, is clearly seen.

#### WHAT WE CLAIM IS:—

1. Biocidal compositions comprising a polymeric quaternary ammonium compound as hereinbefore defined and an isothiazolin - 3 - one compound having the general formula



wherein R represents a hydrogen atom, a halogen atom, a  $C_1-C_4$  alkyl group or a cyano group;

25  $R_1$  represents a  $C_1-C_4$  alkylsulphinyl group, an aralkylsulphinyl group containing up to 8 carbon atoms, a  $C_1-C_4$  alkylsulphonyl group or an aralkylsulphonyl group containing up to 8 carbon atoms where R is a cyano group;

30  $R_1$  represents a hydrogen atom, a halogen atom, an aralkyl group containing up to 8 carbon atoms or a  $C_1-C_4$  halogeno alkyl group when R is a  $C_1-C_4$  alkyl group or a halogen atom provided that  $R_1$  can be a  $C_1-C_4$  alkyl group when R is a  $C_1-C_4$  alkyl group and  $R_1$  is an aralkyl group containing up to 8 carbon atoms or a  $C_1-C_4$  halogeno alkyl group when R is a hydrogen atom; or

40 R and  $R_1$  taken together represent the divalent group  $-C=CH-CH=CH-$ , the hydrogen atoms of which may be replaced by substituents selected from halogen atoms,  $C_1-C_4$  alkyl groups,  $C_1-C_4$  alkoxy groups, the nitro group and the cyano group.

45 2. Biocidal compositions as claimed in claim 1 wherein the polymeric quaternary ammon-

ium compound is selected from a 60:40 molar copolymer of styrene and trimethyl 2 - methacryloyloxyethyl ammonium chloride, poly-(trimethyl 2 - methacryloyloxyethyl ammonium methosulphate), poly(vinyl benzyl trimethylammonium chloride), cyclic polymer of diallyl dimethylammonium chloride, poly(N-methyl vinylpyridium chloride), poly(vinyl chloroacetate) quaternised with pyridine, copolymers of poly(vinyl chloroacetate) and vinyl acetate quaternised with pyridine and the polymer from decamethylene dibromide and  $N,N,N',N'$  - tetramethylhexamethyl diamine.

3. Biocidal compositions as claimed in claim 1 or claim 2 wherein the amounts of polymeric quaternary ammonium compound and isothiazolin - 3 - one compound in the composition are in the range 50:1 to 1:50 by weight respectively.

4. Biocidal compositions as claimed in claim 3 wherein the amounts of polymeric quaternary ammonium compound and isothiazolin - 3 - one compound in the composition are in the range 5:1 to 1:5 by weight respectively.

5. Biocidal compositions as claimed in any one of claims 1 to 4 wherein the isothiazolin-3 - one compound is 1,2 - benzisothiazolin-3 - one.

6. Biocidal compositions as claimed in claim 1 and substantially as hereinbefore described, especially with reference to the foregoing Example.

7. A method for protecting aqueous media against infection by micro-organisms, and for controlling or preventing the proliferation of micro-organisms in aqueous media already infected thereby, which comprises adding to the aqueous media from 1 to 1000 parts per million by weight of a biocidal composition comprising a polymeric quaternary ammonium compound and an isothiazolin - 3 - one compound as claimed in claim 1.

8. A method as claimed in claim 7 and substantially as hereinbefore described, especially with reference to the foregoing Example.

9. Aqueous media whenever protected against infection by micro-organisms, or in which the proliferation of micro-organisms is controlled or prevented, by a method as claimed in Claim 7 or Claim 8.

D. VINCENT,

Agent for the Applicants.